

WATER POLLUTION POTENTIAL OF SPENT OIL SHALE RESIDUES
FROM ABOVE-GROUND RETORTING

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Oil shale resources in the United States cover more than 11 million acres of Colorado, Utah, and Wyoming, and the known petroleum reserve from this source is more than sixty times the proven reserve of crude oil in the United States. If present trends for needs in petroleum in the United States continue, the use of shale oil to supplement crude oil resources becomes likely as a major future development.

In the event the industrial development of oil shale becomes economically feasible, a considerable quantity of retorted shale residue will require disposal. The disposition of spent shale in a way to prevent water pollution will become a problem for industry. Because a good oil shale yields only 25 to 30 gallons of oil per ton of rock, from 85 to 90% of the weight of the original rock appears as spent shale. Some of the precipitation falling on exposed spent oil shale residue piles will run off and will contain dissolved material leached from these piles. Depending on both the concentration and composition of this runoff water, surface streams and possibly some ground waters may be polluted to some extent. The purpose of this project was to determine the water pollution potential of these exposed oil shale residue piles.

The spent oil shale residues investigated were the waste products from 3 pilot plant processes. The processes were: (1) the U.S. Bureau of Mines Gas Combustion Retorting Process, (2) the Union Oil Company Retorting Process, and (3) the TOSCO retorting process which will henceforth be abbreviated respectively USBM, UOC, and TOSCO. The oil shale from all 3 pilot plants came from the Piceance Basin near Rifle, Colorado.

The investigations included the determination of the physical properties of the oil shale retorting residues, and chemical (concentration and composition of dissolved inorganic solids) parameters after blending, shaking, percolation, and simulated precipitation-runoff experiments.

Following are the physical properties of the various oil shale residues:

oil shale residue	USBM	TOSCO	UOC	Raw
geometric mean size, cm	0.205	0.0070		
geometric standard deviation	8.05	3.27		
particle shape factor	0.0526	0.097		
bulk density, g/cc	1.44	1.30	1.80	
solids density, g/cc	2.46	2.49	2.71	2.34
porosity	0.41	0.47	0.33	
permeability, cm ²	3.46×10^{-9}	2.5×10^{-10}		
maximum size, cm	<3.81	<0.476	90	
minimum size, cm	>0.00077	>0.00077	30	

The relationship between geometric mean size, geometric standard deviation of the particle size distribution, particle shape factor, porosity, and permeability is given by equation 107 of reference (1).

With regard to permeability, experiments were run on the TOSCO shale to determine the relationship between saturation and relative permeability. For the solution of this problem, it is more convenient to express relative permeability as a function of capillary pressure, and then using certain approximations, obtain the relationship between relative permeability and capillary pressure (2). For the TOSCO shale the relationship obtained was

$$K_{rw} = S^{3.34} \quad (1)$$

where

K_{rw} = relative permeability, dimensionless
 S^{rw} = fractional saturation, dimensionless.

The saturation moisture content of the TOSCO oil shale residue is 38% by weight ($S = 1$ and $K_{rw} = 1$ when the moisture content is 38%). The value of the exponent in equation (1) indicates that the pore size distribution is quite uniform (A value of 3 is indicative of a completely uniform pore size distribution).

To determine the kind and maximum quantity of dissolved solids leachable, 3 experiments were devised. The first experiment was the blender experiment and consisted of taking a 100 gram sample of the shale which passed the No. 40 sieve, and mixing it with 250 ml of distilled water in a blender. The mixture was then removed from the blender and 750 ml of distilled water added. The mixture was then filtered using a vacuum system with a Büchner funnel and No. 40 Whatman filter paper. The filtrate was then refiltered and the resulting solution placed in a plastic bottle for storage until a chemical analysis could be completed.

The second experiment was the shaker experiment and consisted of taking a 100 gram sample of the shale which passed the No. 40 sieve and placing it in a one gallon container to which 1 liter of distilled water was added. The container was then shaken manually for 5 minutes. The resulting mixture was then filtered using a vacuum system and a Büchner funnel and No. 40 Whatman filter paper. The filtrate was then refiltered and the resulting solution placed in a plastic bottle for storage until a chemical analysis could be completed.

The conductance of each solution was obtained, and a chemical analysis completed on the TOSCO samples. These results are given in Table 1.

Table 1 - Blender and Shaker Experimental Results

Sample	Conductance		Concentration (mg/l)								Test
	(μmhos / cm @ 25°C)		Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ⁼	Cl ⁻	
	Blender	Shaker									
Raw	310	300	-	-	-	-	-	-	-	-	-
USBM	1,000	920	-	-	-	-	-	-	-	-	-
TOSCO	1,770	1,640	165	32	114	27.3	20.2	5.6	730	7.6	Blender
Total mg/l	1,102	1,154	206	10	102	30.9	19.5	5.1	775	5.8	Shaker

Considering differences in composition (due to sampling), the blender and shaker experiments yield a filtrate of approximately the same concentration and composition.

To determine the quantities of dissolved solids leachable by percolation, a percolation experiment was conducted on the TOSCO shale. The apparatus for the experiment consisted of a plastic column 120 cm in length and 10 cm in diameter. The column was filled with 12,500 grams of the TOSCO spent shale, and a constant head of

2 cm maintained on the top of the column. A small outlet, 0.5 cm in diameter, was located at the bottom of the column to provide a means of collecting any leachate.

The first leachate was observed 14 days after the water was originally applied. For the following 28 days, volumes of leachate were collected at various time intervals until a total of 4.6 liters had been percolated and collected.

The volume and conductance of each leachate sample collected was determined. The first 8 samples were analyzed for Ca^{++} , Mg^{++} , Na^+ , SO_4^{--} and Cl^- . These results are given in Table 2.

Table 2 - Experimental Results of the Percolation Experiment on TOSCO Shale

Volume of leachate sample (cc)	Total Volume of leachate (cc)	Conductance of sample ($\mu\text{mhos/cm}$ @ 25°C)	Concentration (mg/l) of sample				
			Na^+	Ca^{++}	Mg^{++}	SO_4^{--}	Cl^-
254	254	78,100	35,200	3,150	4,720	90,000	3,080
340	594	61,600	26,700	2,145	3,725	70,000	1,900
316	910	43,800	14,900	1,560	2,650	42,500	913
150	1,060	25,100	6,900	900	1,450	21,500	370
260	1,320	13,550	2,530	560	500	8,200	205
125	1,445	9,200	1,210	569	579	5,900	138
155	1,600	7,350	735	585	468	4,520	138
250	1,850	6,825	502	609	536	4,450	80
650	2,500	5,700	-	-	-	-	-
650	3,150	4,800	-	-	-	-	-
650	3,800	4,250	-	-	-	-	-
760	4,560	3,850	-	-	-	-	-

The results of the column experiment indicate that

- (1) the dissolved solids are quite readily leached from the column, and
- (2) the concentrations of the various ionic species are quite high, but when the amount of dissolved solids leached from the column per 100 grams of shale is compared to that of the blender and shaker experiments, the results are quite similar. This is indicated in Table 3.

Table 3 - Mass of Various Ions in mg Leached per 100 Grams of TOSCO Shale

Ion	Test		
	Shaker	Blender	Percolation
Ca^{++}	102	114	64
Mg^{++}	31	27	40
Na^+	206	165	258
SO_4^{--}	775	728	675
Cl^-	5	8	18
Total	1,119	1,042	1,055

A computer program has been developed which gives "order of magnitude" results for predicting the concentrations of the effluent from the column. The program is set up to consider a three-phase system. The phases are (1) an exchange phase, (2) a solution phase, and (3) a crystalline salt phase. The program uses relationships developed by Gapon, and considers CaSO_4 as the moderately soluble salt.

The procedure is as follows (3). A volume of initial solution equal to the volume of solution contained in each soil segment is brought into equilibrium with the first segment. By alternately holding the shale phase and the crystalline salt phase (CaSO_4) constant, and by making successive approximations on the Gapon equations, the equilibrium solution for the segment may be calculated. The resulting solution is then equilibrated with a second soil segment, and the procedure repeated until the equilibrium solutions have been equilibrated with all soil segments. The concentration of the solution ions is then printed out.

A second volume of the initial solution is now brought into equilibrium with the first soil segment and the procedure continues until the desired amount of solution is percolated through the soil profile.

Pilot studies using TOSCO unweathered spent oil shale residue were carried out on Colorado State University's Rainfall-Runoff Experimental Facility. The model used for this study had the following characteristics. There were approximately 68 tons of the TOSCO unweathered spent shale placed in a pile 80 feet long, 8 feet wide at the maximum depth of 2 feet and 12 feet wide at the surface. This shale was placed on a 0.75% slope. For the first series of experiments, the surface (top 3 in.) had an in-place density of 83 lb/ft³. The density of the shale below the surface was only 54 lb/ft³. At 4-inch layer of sand was placed below the shale to collect any percolation water. An impermeable plastic barrier was placed below the sand filter and along the sides of the facility to insure that all percolation water was caught. Percolation water from the sand drain was collected in a 50 gallon drum.

Artificial rainfall was applied by a system of nozzles spraying into the air over the facility. The system had the capability of producing rainfall intensities from about 1/2 inch per hour to over 2.5 inches/hour.

Rainfall mass curves were obtained from a recording-type rain gage. The surface runoff was measured by an H-flume with a standard float gage. After passing through the flume, the runoff water was diverted to a small settling basin where it evaporated.

Three access tubes for use of a neutron moisture probe were installed in the middle of the shale at 20, 40, and 60 feet from the upstream end of the facility. Four thermistors were installed 60 feet downstream to monitor the temperature of (1) the air, (2) the surface of the shale, and (3) the shale at depths of one and two feet below the surface.

In the first 9 experiments (3 from natural rainfall, 6 from artificial rainfall), the total water applied amounted to over 26 inches in a 48 day period, or nearly two years of precipitation for the oil shale area.

From the first series of experiments, it was determined that the concentration and composition of total dissolved solids was dependent on several variables, including surface moisture, rainfall intensity, length of overland flow, kinematic viscosity of runoff water, slope, and time since beginning of runoff.

Table 4 gives results of chemical analyses conducted on samples obtained when the runoff rate had reached hydraulic equilibrium (hydraulic equilibrium is reached when runoff rate equals rainfall rate). Only the major constituents are given. Other ions analyzed for but not detected include Cu^{++} , Zn^{++} , Al^{+++} , Fe^{++} , Cr^{+6} , Br^- , F^- , and I^- . The maximum concentration's observed were: K^+ , 30 mg/l; NO_3^- , 9 mg/l; and PO_4^{3-} , 5 mg/l.

Table 4 - Results of Chemical Analyses Conducted on Samples Taken at the Beginning of Hydraulic Equilibrium

Test No.	Rainfall and Runoff Rate, in/hr	Conductivity $\mu\text{mhos/cm @ } 25^{\circ}\text{C}$	Concentration, me/l					
			pH	Na^{+}	Ca^{++}	Mg^{++}	$\text{SO}_4^{=}$	HCO_3^{-}
4	0.55	223	8.203	0.34	1.17	0.20	1.46	0.32
5	0.44	785	8.048	0.67	4.71	0.94	6.04	0.31
6	1.00	425	7.875	0.40	2.37	0.34	2.97	0.34
7	1.72	745	8.167	1.68	3.20	0.62	5.53	0.31
8	2.20	430	8.241	1.70	1.80	0.42	3.81	0.32

Figure 1 shows the effect of drying (before a rainfall event) on the rate at which dissolved solids are leached from the oil shale residue surface during a simulated storm. After a simulated rainfall event, the surface moisture content of the oil shale retorting residue is a maximum (38% by weight). Subsequent drying of this wet surface causes the movement of water from the interior to the surface by capillary action. On reaching the surface, the water evaporates leaving behind a white deposit that is clearly visible on the black surface. This deposit is dissolved during the next rainfall event with the result that both concentration and composition of the dissolved solids in the runoff water vary with time and depend on the amount of drying prior to the rainfall event.

A 10 gram sample of this white deposit was dissolved in a liter of water, and an analysis was made for the major constituents with the following results:

Conductance, $\mu\text{mhos/cm at } 25^{\circ}\text{C}$	Concentration, me/l			
	Na^{+}	Mg^{++}	Ca^{++}	$\text{SO}_4^{=}$
28,500	580	30	10	740

The hydrologic parameters include rainfall intensity, length of overland flow, kinematic viscosity of runoff water, and surface slope. For the model used in this study, the surface slope was the same for all runs. All of these hydrologic parameters are included in the average depth of overland flow, \bar{D} . The average depth of overland flow (in feet) is given by

$$\bar{D} = 3/4 \left[\frac{3iLv}{43,200 \text{ gs}} \right]^{1/3} \quad (2)$$

where

- i = rainfall intensity, inches/hr
- L = length of overland flow, feet
- v = kinematic viscosity, ft^2/sec ($v = 1.088 \times 10^{-5} \text{ ft}^2/\text{sec}$ at 20°C)
- g = acceleration of gravity, 32.2 ft/sec^2
- s = slope, dimensionless ($s = 0.0075$ for all experiments)

43,200 is a unit conversion factor, $\frac{(\text{inch})(\text{seconds})}{(\text{foot})(\text{hour})}$

In order to develop a relationship between \bar{D} and the dissolved solids concentration, the following approach was used. On reciprocal paper the time since beginning of runoff was plotted versus conductance for each run and the value of conductance for the respective runs at infinite time obtained. This value was then plotted versus \bar{D} and using the approximation developed from the data that

dissolved solids in mg/l (0.6) (specific conductance @ 25°C in $\mu\text{mhos/cm}$), the relationship given by equation (3) was developed.

$$(\text{dissolved solids concentration @ infinite time}) = \frac{1.0 \times 10^{-3}}{\bar{D} \cdot 1.86} \quad (3)$$

As mentioned previously, both the concentration and composition of the runoff water varied with time. In general, at the beginning of a run, Na^+ constituted the greatest portion of the cations, while near the end of the run (all experiments extended over approximately four hours) the runoff water approached 100% Ca^{++} in cation concentration. The anion concentration was due almost entirely to SO_4^- .

In order to determine the amount of sediment transported by the runoff water from the shale surface, the following procedure was adopted. An Imhoff cone was filled with 1 liter of runoff sample and allowed to settle for 24 hours. Assuming the settleable matter had a bulk density of 1.30 grams/cc, the settleable solids in mg/l could be determined. By plotting runoff volume times concentration versus time the amount of sediment moved during a given run could be determined. The sediment transported varied from 0.0081 lbs/[(ft²)(hr)] to 0.083 lbs/[(ft²)(hr)] for the series of runs. A particle size distribution was also obtained on the sediment. All of the sediment sampled passed the No. 200 sieve (0.074 mm opening) and had an average size of 0.032 mm.

To account for the water, a water balance was made on each run. These results are given in Table 5.

Table 5 - Water Balance Data

Run	Volume of Water Applied (ft ³)	Volume of Water Runoff (ft ³)	Volume of water Stored (ft ³)	
			Calculated	Observed
4	179	173	+ 6	+ 9
5	160	148	+12	+14
6	350	350	0	+10
7	480	500	-20	+20
8	780	755	+25	+19

The volume of water applied is simply the average rainfall intensity multiplied by the time of application times the area of application. The volume of runoff water can be determined from the hydrograph recorded by the stage recorder. Because no allowance was made for evaporation, the calculated volume of water stored is simply the volume of water applied minus the amount of runoff water. The observed volume of water stored was obtained by multiplying the area of application by the average rainfall intensity times the observed time for the surface of the shale to become wet (at best this observed time would be within $\pm 10\%$).

As indicated from the data, the volume of water stored is quite small. This is also indicated by the change in moisture within the shale as determined by use of a neutron moisture probe. At one foot below the surface, the total change in moisture from the beginning of the first test (natural rainfall) to the last test (test No. 8) was less than 3% for those stations located 20 and 40 ft downstream, and less than 8% for the station located 60 ft downstream. At 1 foot 6 inches below the surface the change in moisture at the 20 ft and 40 ft stations was less than 2%, and for the station located 60 feet downstream the change was less than 12%.

Thermistors located 60 feet downstream indicated temperatures within the shale remained relatively constant between 20-24°C throughout the duration of the experiments. However, the dark color of the spent shale caused temperatures as high as 77°C to be measured on the surface. Temperatures this high could be lethal to germinating seeds.

After the series of nine tests were completed, the bulk density of the spent shale was increased by use of mechanical compacters, and another series of experiments conducted. Results of these experiments are not yet available.

Experiments using artificial snow will be conducted on the shale in late 1970 and early 1971. One natural snowfall has produced conductances in the runoff water as high as 450 $\mu\text{mhos/cm}$ @ 25°C. This conductance was obtained, however, when over half of the snow had melted. Thus, conductances higher than this may occur.

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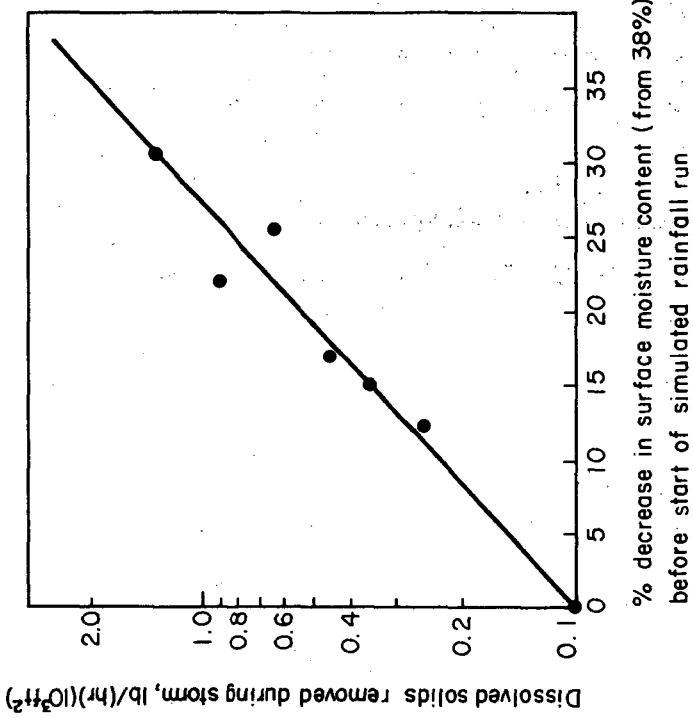


Figure 1 - Leachable Dissolved Solids versus Extent of Drying before Simulated Rainfall Event.